

PATENT ABSTRACTS OF JAPAN

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(54) HIGH HEAT-RESISTANT POLYMER ELECTROLYTE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high heat-resistant polymer electrolyte being excellent in a heat-resistance, an oxidation resistance and a conductivity.

SOLUTION: A perfluoro based polymer compound having a functional group capable of being a strongly acidic cross-linking group such as sulfonyl halide or a compound in which a cross-linking agent having a functional group capable of being a strongly acidic cross-linking group such as sulfonamide at the end of a molecule is added to such perfluoro based polymer compound is subjected to a cross-linking reaction. Thereby, the perfluoro based polymer compound is cross-linked by the strongly acidic cross-linking group comprising vinyl sulfonylimide.

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CLAIMS

[Claim(s)]

[Claim 1] The high thermally stable polymer electrolyte characterized by constructing the bridge over a perfluoro system high molecular compound through a strong acid nature bridge formation radical.

[Claim 2] The high thermally stable polymer electrolyte characterized by said strong acid nature bridge formation radical being at least one chosen from bis-sulfonylimide, sulfonyl carbonyl imide, bis-carbonyl imide, and bis-sulfonyl methylene.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a high thermally stable polymer electrolyte suitable as an electrolyte membrane used for a fuel cell, water electrolysis, halide acid electrolysis, brine electrolysis, an oxygen enricher, a humidity sensor, a gas sensor, etc. in more detail about a high thermally stable polymer electrolyte.

[0002]

[Description of the Prior Art] Solid-state polyelectrolytes are solid-state polymeric materials which have electrolyte radicals, such as a sulfonic group, in a macromolecule chain, since it combines with specific ion firmly or they have the property which penetrates a cation or an anion alternatively, are fabricated a particle, fiber, or in the shape of film, and are used for various kinds of applications.

[0003] For example, a polymer electrolyte fuel cell is a cell which takes out the chemical energy generated in case prepare the electrode of a pair in both sides of an electrolyte membrane, the fuel gas containing hydrogen, such as reformed gas, is supplied to one electrode (fuel electrode), the oxidizer gas containing oxygen, such as air, is supplied to the electrode (air pole) of another side and a fuel oxidizes as direct electrical energy. The solid-state polyelectrolyte film which has proton conductivity is used for the polymer electrolyte fuel cell as an electrolyte membrane.

[0004] Moreover, an SPE electrolytic decomposition process is an approach of manufacturing hydrogen and oxygen by electrolyzing water, it replaces with the conventional alkali water solution as an electrolyte, and the solid-state polyelectrolyte film which has proton conductivity is used.

[0005] As a solid-state polyelectrolyte used for such an application, the perfluoro system electrolyte of not constructing [which is represented by Nafion (a trademark, Du Pont make)] a bridge is known, for example. Since chemical stability is very high, the object for prizes of the perfluoro system electrolyte is carried out as an electrolyte membrane used under severe conditions, such as a fuel cell and SPE electrolysis.

[0006] Moreover, a sulfonyl halide radical is introduced into an aromatic series polyether ketone, the sulfonyl halide radical and the amine system cross linking agent of the UV effectiveness mold which were introduced are made to react, and the bridge formation mold hydrocarbon system electrolyte membrane obtained by subsequently carrying out crosslinking reaction of the amine system cross linking agent is indicated by U.S. Pat. No. 5741408.

[0007] Furthermore, the screw (perfluoroalkyl sulfonyl) imide radical is proposed by 203-208 pages (Journal of Fluorine Chemistry) of the 72nd volume (1995) of journal OBU fluorine chemistry, the 145th volume (Journal of Electro-Chemical Society) of journal OBU electrochemical SOSAIAT1, and No.1 (1998)107-109 page as a new acid radical. The various screw (perfluoroalkyl sulfonyl) imide polymers and screw (perfluoroalkyl sulfonyl) imide compound which present strong acid nature are reported. Moreover, the polymer which the sulfonyl carbonyl imide anion contained by high concentration is indicated by JP, 9-263637, A.

[0008]

[Problem(s) to be Solved by the Invention] By the way, as for the polymer electrolyte fuel cell, it is known that generating efficiency will become high, so that the operating

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temperature of a cell becomes high. Moreover, although the electrode catalyst of a platinum system is included in the electrode joined by both sides of a solid-state polyelectrolyte, even if platinum is the carbon monoxide of a minute amount, poisoning of it is carried out, and it becomes the cause of reducing the output of a fuel cell. And it is known that low temperature will become remarkable [poisoning by the carbon monoxide of an electrode catalyst].

[0009] Therefore, in the polymer electrolyte fuel cell using the gas containing the carbon monoxide of a minute amount, such as methanol reformed gas, as fuel gas, to make operating temperature high for reduction of carbon monoxide poisoning of efficient-izing and an electrode catalyst is desired.

[0010] Moreover, in water electrolysis, although total energy required for the electrolysis of water does not change with temperature so much, becoming so small that the minimum electrical potential difference required for the electrolysis of water, i.e., theoretical decomposition voltage, becoming an elevated temperature is known. Therefore, if heat energy can be supplied to a system and a electrolysis reaction can be made to perform in an elevated temperature from the exterior, consumption of expensive electrical energy can be cut down and it is advantageous in respect of effectiveness.

[0011] However, the perfluoro system electrolyte represented by Nafion has the property for thermal resistance to be low in order not to construct a bridge, and to carry out a creep above 130 degrees C which it is near the glass transition temperature. Therefore, when a perfluoro system electrolyte was used for a fuel cell or an SPE electrolytic device, operating temperature needed to be made into 100 degrees C or less, and there was a problem that it could not be used at an advantageous elevated temperature in respect of prevention of poisoning of the electrode catalyst by the carbon monoxide or effectiveness. Moreover, when the perfluoro system electrolyte increased the amount of installation of an electrolyte radical too much in order not to construct a bridge, and to raise conductivity, it swelled or solubilized in water remarkably, and the membranous design degree of freedom was also sharply limited to it.

[0012] on the other hand — a perfluoro system electrolyte — **** — if last thing is made, since a flow of a hot macromolecule chain will be controlled, it is thought to the formation of an elevated-temperature-proof creep of a perfluoro system electrolyte that it is effective. Furthermore, the design degree of freedom of conductive improvement improves, without solubilizing, even if it increases the amount of installation of a membranous electrolyte radical according to bridge formation. However, the chemical stability of structure, therefore bridge formation with a principal chain are difficult for a perfluoro system electrolyte.

[0013] On the other hand, if the approach currently indicated by U.S. Pat. No. 5741408 is diverted to some other purpose, it prepares for the perfluoro system electrolyte and a high electrolyte radical or a reactant electrolyte radical precursor, and a reactant amine system cross linking agent are made to react, it is possible to also make a perfluoro system electrolyte construct a bridge. However, by this approach, the amount of the electrolyte radical contained in a perfluoro system electrolyte decreases, and there is a problem that conductivity falls.

[0014] Moreover, since parts for the principal part including a cross linking agent consist of hydrocarbon structures, the bridge formation mold hydrocarbon system electrolyte itself currently indicated by U.S. Pat. No. 5741408 does not have the oxidation resistance in an elevated temperature, and if it remains as it is, it cannot be used at an elevated temperature.

[0015] Furthermore, it is reported to the 145th volume of journal OBU electrochemical SOSAIATI, and No.1 (1998)107-109 page by by combining the perfluoro frame of a screw (perfluoroalkyl sulfonyl) imide radical and Mr. Nafion that the screw (perfluoroalkyl sulfonyl) imide polymer which has the almost same proton conductivity as Nafion is obtained. However, since each of these compounds is compounds of the mold non-constructing a bridge, a problem is in thermal resistance like Nafion. Moreover, there is no example which applied such a functional group to bridge formation of a perfluoro system electrolyte.

[0016] Moreover, since it contains a strong acid radical by high concentration, the polymer

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(H⁺ type) shown in JP, 9-263637, A is fundamentally meltable in water, as an electrolyte for fuel cells, remains as it is before thermal resistance, and is not applicable to it.

[0017] The technical problem which this invention tends to solve is excellent in thermal resistance and oxidation resistance, and is to offer the high thermally stable polymer electrolyte which moreover has high conductivity.

[0018]

[Means for Solving the Problem] The high thermally stable polymer electrolyte built over this invention in order to solve the above-mentioned technical problem makes it a summary to construct the bridge over a perfluoro system high molecular compound through a strong acid nature bridge formation radical.

[0019] Here, a strong acid nature bridge formation radical means what the structure of the point after bridge formation constructing a bridge presents strong acid nature where water is included. Although what has various structures is mentioned as a bridge formation radical which has such a property, as a strong acid nature bridge formation radical, bis-sulfonylimide, sulfonyl carbonyl imide, bis-carbonyl imide, bis-sulfonyl methylene, etc. are suitable. In addition, it is not especially limited by the point constructing a bridge that what is necessary is just to be in either of the chains of a perfluoro system high molecular compound.

[0020] Since the bridge is constructed over the perfluoro system high molecular compound through the strong acid nature bridge formation radical, a flow of a hot molecule is controlled and the high thermally stable polymer electrolyte concerning this invention can raise elevated-temperature-proof creep nature sharply.

[0021] Moreover, since the point itself constructing a bridge is strong acid nature, even if it makes crosslinking density increase, electrolytic conductivity is not reduced greatly. Furthermore, since the macromolecule chain consists of perfluoro systems, hot oxidation resistance does not pose a problem, either.

[0022] Therefore, when this is used for a fuel cell or an SPE electrolytic device, even if it is under a high temperature service 130 degrees C or more, it can operate to stability, and effectiveness can be raised by leaps and bounds. And the sag resulting from poisoning by the carbon monoxide of the electrode catalyst which poses a problem in the methanol-reforming mold fuel cell is sharply mitigable with such elevated-temperature operation.

[0023]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail. The high thermally stable polymer electrolyte concerning this invention is equipped with the strong acid nature bridge formation radical and the perfluoro system high molecular compound over which the bridge was constructed through the strong acid nature bridge formation radical.

[0024] Here, a strong acid nature bridge formation radical needs to mean what the structure of the point after bridge formation constructing a bridge presents strong acid nature as mentioned above, and the functional group before bridge formation does not necessarily need to be strong acid nature. Specifically as a strong acid nature bridge formation radical for making a perfluoro system high molecular compound construct a bridge, bis-sulfonylimide (-SO₂-NH-SO₂-) is suitable.

[0025] Bis-sulfonylimide discovers high proton conductivity equivalent to Nafion by combining with a perfluoro frame. This is because H which the electron contributed to N-H coupling was pulled by F with big electronegativity, moved to the perfluoro frame side, and has been combined with the point constructing a bridge becomes is easy to be emitted as a proton by making a perfluoro system high molecular compound construct a bridge through bis-sulfonylimide.

[0026] Therefore, the strong acid nature bridge formation radical for making a perfluoro system giant molecule construct a bridge is not restricted to bis-sulfonylimide, and if it is a bridge formation radical equipped with the structure to which it is easy to move an electron from the point constructing a bridge, it can turn into a "strong acid nature bridge formation radical" which says all by this invention.

[0027] As other suitable examples of a strong acid nature bridge formation radical, bis-sulfonyl methylene (-SO₂-CH₂-SO₂-), bis-carbonyl imide (-CO-NH-CO-), sulfonyl carbonyl imide (-CO-NH-SO₂-), etc. are mentioned, for example.

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[0028] Although especially the structure of the perfluoro system high molecular compound which constitutes a part for the principal part of the high thermally stable polymer electrolyte concerning this invention is not limited, especially the perfluoro system electrolyte polymer which has strong acid nature functional groups, such as a sulfonic group, a carboxylic-acid radical, a bis-sulfonylimide radical, and a phosphonic acid radical, in a side chain, its precursor, derivative, etc. are suitable for it. Moreover, the macromolecule chain may have which structure of the shape of a straight chain, and the letter of branching. Moreover, the point constructing a bridge should just be in either of the chains of a perfluoro system high molecular compound. That is, the bridge may be constructed with the principal chain and may be constructed with the side chain.

[0029] In addition, the polyelectrolyte excellent in thermal resistance is obtained so that crosslinking density becomes large in the case of this invention, but when crosslinking density becomes excessive, migration of water and a water molecule is barred and there is an inclination to reduce proton conductivity on the contrary. Therefore, crosslinking density should just choose the optimal value according to thermal resistance, conductivity, etc. which are required of a high thermally stable polymer electrolyte.

[0030] Moreover, through one kind of strong acid nature bridge formation radical, the bridge may be constructed over the perfluoro system high molecular compound, or may be constructed over the perfluoro system high molecular compound to the high thermally stable polymer electrolyte concerning this invention through two or more sorts of strong acid nature bridge formation radicals.

[0031] Next, the manufacture approach of the high thermally stable polymer electrolyte concerning this invention is explained. The high thermally stable polymer electrolyte concerning this invention can be obtained by carrying out crosslinking reaction of the perfluoro system macromolecule chains through direct or a cross linking agent.

[0032] Therefore, it is necessary to equip the perfluoro system high molecular compound which constitutes a part for the principal part of a high thermally stable polymer electrolyte with the functional group (for this to be hereafter called "functional group A") which can turn into a strong acid nature bridge formation radical with a cross linking agent in response to either of the chains which constitute a perfluoro system high molecular compound.

[0033] Specifically as a functional group A with which a perfluoro system high molecular compound is equipped, a sulfonyl halide radical, a carbonyl halide radical, a carboxylate radical, etc. are mentioned as an example with these suitable derivatives. Since especially a sulfonyl halide radical turns into a strong acid radical easily and can give high conductivity to an electrolyte if this is hydrolyzed even if it is the case where it is not consumed by bridge formation, it is suitable as a functional group A.

[0034] moreover, as a perfluoro system high molecular compound which has such a functional group A concrete — tetrafluoroethylene and a perfluoro (4-methyl -3, 6-dioxa oct-7-en) sulfonyl full ora — the copolymer of the id — tetrafluoroethylene and a perfluoro (3-OKISA-PENTA-4-en) sulfonyl full ora — a copolymer with the id — tetrafluoroethylene and a perfluoro (4-OKISA hexa-5-en) sulfonyl full ora — a copolymer with the id — These derivatives, such as a copolymer of tetrafluoroethylene and perfluoro (4-OKISA-5 HEKISE noil chloride), are mentioned as a suitable example.

[0035] In addition, especially the concentration of the functional group A with which a perfluoro system high molecular compound is equipped is not limited, and the compound which has the optimal concentration should just be used for it according to thermal resistance, conductivity, etc. which are required of a high thermally stable polymer electrolyte. Since the control range of crosslinking density generally becomes large so that the concentration of a functional group A becomes high, there is an advantage that the various polyelectrolytes with which thermal resistance differs from conductivity are obtained. On the other hand, if the concentration of a functional group A decreases too much, crosslinking density will fall and thermal resistance will become inadequate. concrete — as the concentration of a functional group A — 4×10^{-3} mol/g — it is 2×10^{-3} mol/g — 1×10^{-5} mol/g preferably 1×10 to 6 mol/g.

[0036] Moreover, one kind of functional group A may be contained in the perfluoro system high molecular compound before bridge formation, or two or more sorts of functional groups

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A may be contained in it. Furthermore, the single perfluoro system high molecular compound which has one sort or two sorts or more of functional groups A may be made to construct a bridge, or the same or two or more sorts of perfluoro system high molecular compounds equipped with a different functional group A may be mixed by the ratio of arbitration, and this may be made to construct a bridge.

[0037] Next, a cross linking agent is explained. It is necessary to have two or more functional groups which it reacts with the functional group A which a perfluoro system high molecular compound has, and can construct a bridge into 1 molecule as a cross linking agent, and, moreover, at least one of them needs to use what consists of a functional group (this is hereafter called "functional group B") which can turn into a strong acid nature bridge formation radical. What is especially equipped with the two or more above functional groups B into one molecule is suitable as a cross linking agent.

[0038] Specifically as a functional group B with which a cross linking agent is equipped, a sulfonamide radical ($\text{NH}_2\text{-SO}_2\text{-}$), sulfonyl (N-trimethylsilyl) imide sodium salt $(\text{CH}_3)_3\text{Si-N}(\text{Na})\text{-SO}_2\text{-}$, an amide group ($\text{NH}_2\text{-CO-}$), etc. are mentioned as an example with these suitable derivatives. However, even if it is not sodium about sulfonyl (N-trimethylsilyl) imide sodium salt, alkali metal, alkaline earth metal, and hydrogen are sufficient.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a high thermally stable polymer electrolyte suitable as an electrolyte membrane used for a fuel cell, water electrolysis, halide acid electrolysis, brine electrolysis, an oxygen enricher, a humidity sensor, a gas sensor, etc. in more detail about a high thermally stable polymer electrolyte.

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PRIOR ART

[Description of the Prior Art] Solid-state polyelectrolytes are solid-state polymeric materials which have electrolyte radicals, such as a sulfonic group, in a macromolecule chain, since it combines with specific ion firmly or they have the property which penetrates a cation or an anion alternatively, are fabricated a particle, fiber, or in the shape of film, and are used for various kinds of applications.

[0003] For example, a polymer electrolyte fuel cell is a cell which takes out the chemical energy generated in case prepare the electrode of a pair in both sides of an electrolyte membrane, the fuel gas containing hydrogen, such as reformed gas, is supplied to one electrode (fuel electrode), the oxidizer gas containing oxygen, such as air, is supplied to the electrode (air pole) of another side and a fuel oxidizes as direct electrical energy. The solid-state polyelectrolyte film which has proton conductivity is used for the polymer electrolyte fuel cell as an electrolyte membrane.

[0004] Moreover, an SPE electrolytic decomposition process is an approach of manufacturing hydrogen and oxygen by electrolyzing water, it replaces with the conventional alkali water solution as an electrolyte, and the solid-state polyelectrolyte film which has proton conductivity is used.

[0005] As a solid-state polyelectrolyte used for such an application, the perfluoro system electrolyte of not constructing [which is represented by Nafion (a trademark, Du Pont make)] a bridge is known, for example. Since chemical stability is very high, the object for prizes of the perfluoro system electrolyte is carried out as an electrolyte membrane used under severe conditions, such as a fuel cell and SPE electrolysis.

[0006] Moreover, a sulfonyl halide radical is introduced into an aromatic series polyether ketone, the sulfonyl halide radical and the amine system cross linking agent of the UV effectiveness mold which were introduced are made to react, and the bridge formation mold hydrocarbon system electrolyte membrane obtained by subsequently carrying out crosslinking reaction of the amine system cross linking agent is indicated by U.S. Pat. No. 5741408.

[0007] Furthermore, the screw (perfluoroalkyl sulfonyl) imide radical is proposed by 203-208 pages (Journal of Fluorine Chemistry) of the 72nd volume (1995) of journal OBU fluorine chemistry, the 145th volume (Journal of Electro-Chemical Society) of journal OBU electrochemical SOSAIAT, and No.1 (1998)107-109 page as a new acid radical. The various screw (perfluoroalkyl sulfonyl) imide polymers and screw (perfluoroalkyl sulfonyl) imide compound which present strong acid nature are reported. Moreover, the polymer which the sulfonyl carbonyl imide anion contained by high concentration is indicated by JP, 9-263637, A.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since the bridge is constructed over the perfluoro system high molecular compound through the strong acid nature bridge formation radical, a flow of a hot macromolecule chain is controlled and the high thermal-resistance solid-state polyelectrolyte concerning this invention is effective in elevated-temperature-proof creep nature improving.

[0117] Moreover, since the point itself constructing a bridge is strong acid nature, even if it makes crosslinking density increase, it is effective in not reducing electrolytic conductivity. When bis-sulfonylimide etc. is especially used as a strong acid nature bridge formation radical, it is effective in the electrolyte equipped with high conductivity and elevated-temperature-proof creep nature being obtained by combining with a perfluoro frame.

[0118] Furthermore, since the macromolecule chain consists of perfluoro systems, it is effective in the high thermally stable polymer electrolyte excellent in hot oxidation resistance being obtained.

[0119] As mentioned above, since the high thermally stable polymer electrolyte concerning this invention is excellent in thermal resistance, oxidation resistance, and conductivity, when this is applied to for example, the fuel cell for mount, or an SPE electrolytic device, it contributes to improvement, efficient-izing, etc. of fuel consumption, and it is very large invention of the effectiveness on industry.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the way, as for the polymer electrolyte fuel cell, it is known that generating efficiency will become high, so that the operating temperature of a cell becomes high. Moreover, although the electrode catalyst of a platinum system is included in the electrode joined by both sides of a solid-state polyelectrolyte, even if platinum is the carbon monoxide of a minute amount, poisoning of it is carried out, and it becomes the cause of reducing the output of a fuel cell. And it is known that low temperature will become remarkable [poisoning by the carbon monoxide of an electrode catalyst].

[0009] Therefore, in the polymer electrolyte fuel cell using the gas containing the carbon monoxide of a minute amount, such as methanol reformed gas, as fuel gas, to make operating temperature high for reduction of carbon monoxide poisoning of efficient-izing and an electrode catalyst is desired.

[0010] Moreover, in water electrolysis, although total energy required for the electrolysis of water does not change with temperature so much, becoming so small that the minimum electrical potential difference required for the electrolysis of water, i.e., theoretical decomposition voltage, becoming an elevated temperature is known. Therefore, if heat energy can be supplied to a system and a electrolysis reaction can be made to perform in an elevated temperature from the exterior, consumption of expensive electrical energy can be cut down and it is advantageous in respect of effectiveness.

[0011] However, the perfluoro system electrolyte represented by Nafion has the property for thermal resistance to be low in order not to construct a bridge, and to carry out a creep above 130 degrees C which it is near the glass transition temperature. Therefore, when a perfluoro system electrolyte was used for a fuel cell or an SPE electrolytic device, operating temperature needed to be made into 100 degrees C or less, and there was a problem that it could not be used at an advantageous elevated temperature in respect of prevention of poisoning of the electrode catalyst by the carbon monoxide or effectiveness. Moreover, when the perfluoro system electrolyte increased the amount of installation of an electrolyte radical too much in order not to construct a bridge, and to raise conductivity, it swelled or solubilized in water remarkably, and the membranous design degree of freedom was also sharply limited to it.

[0012] on the other hand — a perfluoro system electrolyte — **** — if last thing is made, since a flow of a hot macromolecule chain will be controlled, it is thought to the formation of an elevated-temperature-proof creep of a perfluoro system electrolyte that it is effective. Furthermore, the design degree of freedom of conductive improvement improves, without solubilizing, even if it increases the amount of installation of a membranous electrolyte radical according to bridge formation. However, the chemical stability of structure, therefore bridge formation with a principal chain are difficult for a perfluoro system electrolyte.

[0013] On the other hand, if the approach currently indicated by U.S. Pat. No. 5741408 is diverted to some other purpose, it prepares for the perfluoro system electrolyte and a high electrolyte radical or a reactant electrolyte radical precursor, and a reactant amine system cross linking agent are made to react, it is possible to also make a perfluoro system electrolyte construct a bridge. However, by this approach, the amount of the electrolyte radical contained in a perfluoro system electrolyte decreases, and there is a

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problem that conductivity falls.

[0014] Moreover, since parts for the principal part including a cross linking agent consist of hydrocarbon structures, the bridge formation mold hydrocarbon system electrolyte itself currently indicated by U.S. Pat. No. 5741408 does not have the oxidation resistance in an elevated temperature, and if it remains as it is, it cannot be used at an elevated temperature.

[0015] Furthermore, it is reported to the 145th volume of journal OBU electrochemical SOCIETY, and No. 1 (1998) 107-109 page by by combining the perfluoro frame of a screw (perfluoroalkyl sulfonyl) imide radical and Mr. Nafion that the screw (perfluoroalkyl sulfonyl) imide polymer which has the almost same proton conductivity as Nafion is obtained. However, since each of these compounds is compounds of the mold non-constructing a bridge, a problem is in thermal resistance like Nafion. Moreover, there is no example which applied such a functional group to bridge formation of a perfluoro system electrolyte.

[0016] Moreover, since it contains a strong acid radical by high concentration, the polymer (H⁺ type) shown in JP, 9-263637, A is fundamentally meltable in water, as an electrolyte for fuel cells, remains as it is before thermal resistance, and is not applicable to it.

[0017] The technical problem which this invention tends to solve is excellent in thermal resistance and oxidation resistance, and is to offer the high thermally stable polymer electrolyte which moreover has high conductivity.

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MEANS

[Means for Solving the Problem] The high thermally stable polymer electrolyte built over this invention in order to solve the above-mentioned technical problem makes it a summary to construct the bridge over a perfluoro system high molecular compound through a strong acid nature bridge formation radical.

[0019] Here, a strong acid nature bridge formation radical means what the structure of the point after bridge formation constructing a bridge presents strong acid nature where water is included. Although what has various structures is mentioned as a bridge formation radical which has such a property, as a strong acid nature bridge formation radical, bis-sulfonylimide, sulfonyl carbonyl imide, bis-carbonyl imide, bis-sulfonyl methylene, etc. are suitable. In addition, it is not especially limited by the point constructing a bridge that what is necessary is just to be in either of the chains of a perfluoro system high molecular compound.

[0020] Since the bridge is constructed over the perfluoro system high molecular compound through the strong acid nature bridge formation radical, a flow of a hot molecule is controlled and the high thermally stable polymer electrolyte concerning this invention can raise elevated-temperature-proof creep nature sharply.

[0021] Moreover, since the point itself constructing a bridge is strong acid nature, even if it makes crosslinking density increase, electrolytic conductivity is not reduced greatly. Furthermore, since the macromolecule chain consists of perfluoro systems, hot oxidation resistance does not pose a problem, either.

[0022] Therefore, when this is used for a fuel cell or an SPE electrolytic device, even if it is under a high temperature service 130 degrees C or more, it can operate to stability, and effectiveness can be raised by leaps and bounds. And the sag resulting from poisoning by the carbon monoxide of the electrode catalyst which poses a problem in the methanol-reforming mold fuel cell is sharply mitigable with such elevated-temperature operation.

[0023]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail. The high thermally stable polymer electrolyte concerning this invention is equipped with the strong acid nature bridge formation radical and the perfluoro system high molecular compound over which the bridge was constructed through the strong acid nature bridge formation radical.

[0024] Here, a strong acid nature bridge formation radical needs to mean what the structure of the point after bridge formation constructing a bridge presents strong acid nature as mentioned above, and the functional group before bridge formation does not necessarily need to be strong acid nature. Specifically as a strong acid nature bridge formation radical for making a perfluoro system high molecular compound construct a bridge, bis-sulfonylimide (-SO₂-NH-SO₂-) is suitable.

[0025] Bis-sulfonylimide discovers high proton conductivity equivalent to Nafion by combining with a perfluoro frame. This is because H which the electron contributed to N-H coupling was pulled by F with big electronegativity, moved to the perfluoro frame side, and has been combined with the point constructing a bridge becomes is easy to be emitted as a proton by making a perfluoro system high molecular compound construct a bridge through bis-sulfonylimide.

[0026] Therefore, the strong acid nature bridge formation radical for making a perfluoro

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system giant molecule construct a bridge is not restricted to bis-sulfonylimide, and if it is a bridge formation radical equipped with the structure to which it is easy to move an electron from the point constructing a bridge, it can turn into a "strong acid nature bridge formation radical" which says all by this invention.

[0027] As other suitable examples of a strong acid nature bridge formation radical, bis-sulfonyl methylene ($-\text{SO}_2-\text{CH}_2-\text{SO}_2-$), bis-carbonyl imide ($-\text{CO}-\text{NH}-\text{CO}-$), sulfonyl carbonyl imide ($-\text{CO}-\text{NH}-\text{SO}_2-$), etc. are mentioned, for example.

[0028] Although especially the structure of the perfluoro system high molecular compound which constitutes a part for the principal part of the high thermally stable polymer electrolyte concerning this invention is not limited, especially the perfluoro system electrolyte polymer which has strong acid nature functional groups, such as a sulfonic group, a carboxylic-acid radical, a bis-sulfonylimide radical, and a phosphonic acid radical, in a side chain, its precursor, derivative, etc. are suitable for it. Moreover, the macromolecule chain may have which structure of the shape of a straight chain, and the letter of branching. Moreover, the point constructing a bridge should just be in either of the chains of a perfluoro system high molecular compound. That is, the bridge may be constructed with the principal chain and may be constructed with the side chain.

[0029] In addition, the polyelectrolyte excellent in thermal resistance is obtained so that crosslinking density becomes large in the case of this invention, but when crosslinking density becomes excessive, migration of water and a water molecule is barred and there is an inclination to reduce proton conductivity on the contrary. Therefore, crosslinking density should just choose the optimal value according to thermal resistance, conductivity, etc. which are required of a high thermally stable polymer electrolyte.

[0030] Moreover, through one kind of strong acid nature bridge formation radical, the bridge may be constructed over the perfluoro system high molecular compound, or may be constructed over the perfluoro system high molecular compound to the high thermally stable polymer electrolyte concerning this invention through two or more sorts of strong acid nature bridge formation radicals.

[0031] Next, the manufacture approach of the high thermally stable polymer electrolyte concerning this invention is explained. The high thermally stable polymer electrolyte concerning this invention can be obtained by carrying out crosslinking reaction of the perfluoro system macromolecule chains through direct or a cross linking agent.

[0032] Therefore, it is necessary to equip the perfluoro system high molecular compound which constitutes a part for the principal part of a high thermally stable polymer electrolyte with the functional group (for this to be hereafter called "functional group A") which can turn into a strong acid nature bridge formation radical with a cross linking agent in response to either of the chains which constitute a perfluoro system high molecular compound.

[0033] Specifically as a functional group A with which a perfluoro system high molecular compound is equipped, a sulfonyl halide radical, a carbonyl halide radical, a carboxylate radical, etc. are mentioned as an example with these suitable derivatives. Since especially a sulfonyl halide radical turns into a strong acid radical easily and can give high conductivity to an electrolyte if this is hydrolyzed even if it is the case where it is not consumed by bridge formation, it is suitable as a functional group A.

[0034] moreover, as a perfluoro system high molecular compound which has such a functional group A concrete — tetrafluoroethylene and a perfluoro (4-methyl -3, 6-dioxo oct-7-en) sulfonyl full ora — the copolymer of the id — tetrafluoroethylene and a perfluoro (3-OKISA-PENTA-4-en) sulfonyl full ora — a copolymer with the id — tetrafluoroethylene and a perfluoro (4-OKISA hexa-5-en) sulfonyl full ora — a copolymer with the id — These derivatives, such as a copolymer of tetrafluoroethylene and perfluoro (4-OKISA-5 HEKISE noil chloride), are mentioned as a suitable example.

[0035] In addition, especially the concentration of the functional group A with which a perfluoro system high molecular compound is equipped is not limited, and the compound which has the optimal concentration should just be used for it according to thermal resistance, conductivity, etc. which are required of a high thermally stable polymer electrolyte. Since the control range of crosslinking density generally becomes large so that the concentration of a functional group A becomes high, there is an advantage that the various

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polyelectrolytes with which thermal resistance differs from conductivity are obtained. On the other hand, if the concentration of a functional group A decreases too much, crosslinking density will fall and thermal resistance will become inadequate. concrete — as the concentration of a functional group A — 4×10^{-3} mol/g — it is 2×10^{-3} mol/g — 1×10^{-5} mol/g preferably 1×10 to 6 mol/g.

[0036] Moreover, one kind of functional group A may be contained in the perfluoro system high molecular compound before bridge formation, or two or more sorts of functional groups A may be contained in it. Furthermore, the single perfluoro system high molecular compound which has one sort or two sorts or more of functional groups A may be made to construct a bridge, or the same or two or more sorts of perfluoro system high molecular compounds equipped with a different functional group A may be mixed by the ratio of arbitration, and this may be made to construct a bridge.

[0037] Next, a cross linking agent is explained. It is necessary to have two or more functional groups which it reacts with the functional group A which a perfluoro system high molecular compound has, and can construct a bridge into 1 molecule as a cross linking agent, and, moreover, at least one of them needs to use what consists of a functional group (this is hereafter called "functional group B") which can turn into a strong acid nature bridge formation radical. What is especially equipped with the two or more above functional groups B into one molecule is suitable as a cross linking agent.

[0038] Specifically as a functional group B with which a cross linking agent is equipped, a sulfonamide radical ($\text{NH}_2\text{-SO}_2\text{-}$), sulfonyl (N-trimethylsilyl) imide sodium salt (CH_3) ($3 \text{ Si-N (Na)-SO}_2\text{-}$), an amide group ($\text{NH}_2\text{-CO-}$), etc. are mentioned as an example with these suitable derivatives. However, even if it is not sodium about sulfonyl (N-trimethylsilyl) imide sodium salt, alkali metal, alkaline earth metal, and hydrogen are sufficient.

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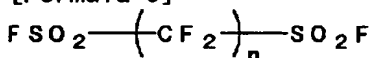
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EXAMPLE

[Example] (Example 1) First according to the following procedures, the cross linking agent was compounded. first -- as the raw material of a cross linking agent -- the end of both ends -- a sulfonyl full ora -- the id -- the perfluoro -1 and 4-disulfo nil FURUORAIDO butane which have a radical were used. The chemical formula of perfluoro -1 and 4-disulfo nil FURUORAIDO butane is shown in the formula (n is 4) of next ** 9.

[0069]

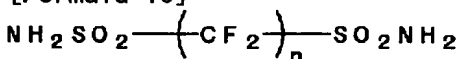
[Formula 9]



[0070] Next, at -78 degrees, the perfluoro -1 and 4-disulfo nil FURUORAIDO butane which are shown in the formula of ** 9 were added into the liquid ammonia of an excessive amount, and were sulfonamide-ized. Subsequently, after returning to the room temperature and removing ammonia, hydrogen chloride gas was made to act and the perfluoro -1 and 4-disulfon amide butane which have a sulfonamide radical in the end of both ends were compounded. The chemical formula of the obtained perfluoro -1 and 4-disulfon amide butane is shown in the formula of next ** 10.

[0071]

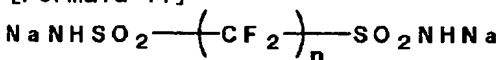
[Formula 10]



[0072] Next, dissolved the sulfonamide compound shown in the formula of ** 10 in the methanol, the equivalent sodium METOKI side was made to act, and sulfonamide sodium salt was compounded. The chemical formula of the obtained sulfonamide sodium salt is shown in the formula of next ** 11.

[0073]

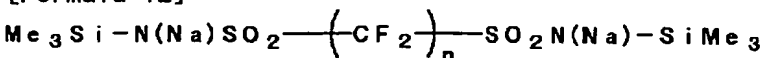
[Formula 11]



[0074] Furthermore, to the sulfonamide sodium salt shown in the formula of ** 11, the hexamethyldisilazane of an amount was made to act at reflux temperature 1.2 times in an acetonitrile, and the target cross linking agent was compounded. The chemical formula of the obtained cross linking agent is shown in the formula of next ** 12.

[0075]

[Formula 12]



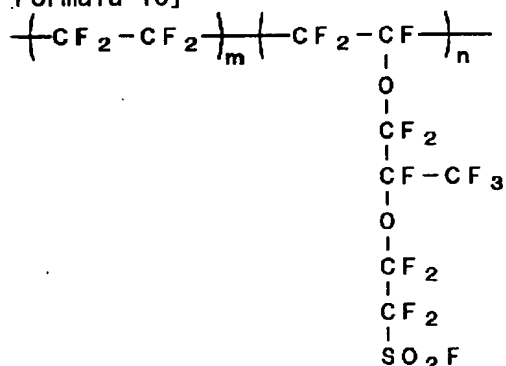
[0076] Next, crosslinking reaction was performed according to the following procedures. the perfluoro system sulfonyl full ora which is an electrolyte precursor before hydrolysis at the perfluoro system high molecular compound used as the raw material of a high thermally stable polymer electrolyte -- the id -- the film (this is hereafter called "PFSF film") was used. the sulfonyl full ora of this PFSF film -- the id -- the concentration (polymer 1g the inner number of mol) of a radical is 9.07×10^{-4} mol/g, and thickness is 50

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micrometers. The chemical formula of the PFSF film used for crosslinking reaction is shown in the formula of next ** 13.

[0077]

[Formula 13]



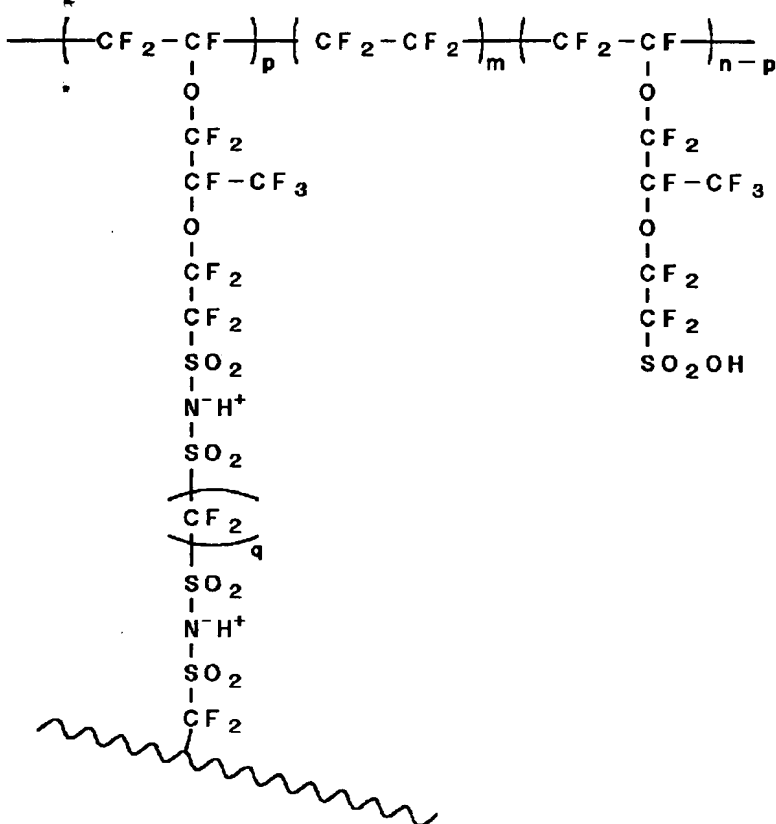
[0078] first, the sulfonyl full ora contained in the PFSF film shown in the formula of ** 13 -- the id -- the cross linking agent which corresponds to ten-mol% (it is 20-mol% in the functional-group base in a cross linking agent) to a radical was dissolved into the acetonitrile. Subsequently, the PFSF film was immersed into the acetonitrile in which the cross linking agent was dissolved, and it heated as it is for 20 hours, and considered as the bridge formation film.

[0079] next, the sulfonyl full ora which heat-treats the obtained bridge formation film at 90 degrees C in a sodium-hydroxide water solution 25%, and hydrolyzes and remains -- the id -- the radical was changed into the sulfonic-acid sodium group. Furthermore, reflux processing of 1 hour was repeated twice in 1-N sulfuric-acid water solution, and the polyelectrolyte film (this is hereafter called "strong acid nature bridge formation electrolyte membrane") over which the bridge was constructed by the strong acid nature bridge formation radical was obtained by changing into a proton mold. The chemical formula of the obtained strong acid nature bridge formation electrolyte membrane is shown in the formula of next ** 14.

[0080]

[Formula 14]

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[0081] In addition, ** 14 formula shows typically the condition that p of n side chains which are carrying out the polymerization to the principal chain which consists of tetrafluoroethylene were consumed by bridge formation. Moreover, the part shown with the wavy line sketches the perfluoro system macromolecule chain which has the same structure as the formula of ** 13 among ** 14 type.

[0082] (Example 2) a sulfonyl full ora -- the id -- according to the same procedure as an example 1, the strong acid nature bridge formation electrolyte membrane was produced to the radical except having used the one-mol % of cross linking agent (it being two-mol% in the functional-group base).

[0083] (Example 3) a sulfonyl full ora -- the id -- according to the same procedure as an example 1, the strong acid nature bridge formation electrolyte membrane was produced except having used the 20-mol % of cross linking agent (it being 40-mol% in the functional-group base) to the radical.

[0084] (Example 4) a sulfonyl full ora -- the id -- according to the same procedure as an example 1, the strong acid nature bridge formation electrolyte membrane was produced except having used the PFSF film whose concentration of a radical is 1.25×10^{-3} mol/g.

[0085] (Example 5) as a cross linking agent -- 3 (CH₃) Si-N(Na)-Si (CH₃)₃ -- a sulfonyl full ora -- the id -- a radical -- receiving -- ten-mol% -- according to the same procedure as an example 3, the strong acid nature bridge formation electrolyte membrane was produced except having used.

[0086] (Example 1 of a comparison) without it makes the PFSF film (however, a sulfonyl full ora id concentration: 9.07×10^{-4} mol/g of a radical, thickness : 50 micrometers) construct a bridge -- as it is -- 25% sodium-hydroxide water solution -- 90 degrees C -- heat-treating -- hydrolyzing -- a sulfonyl full ora -- the id -- the radical was changed into the sulfonic-acid sodium group. Furthermore, reflux processing of 1 hour was repeated twice in 1-N sulfuric-acid water solution, and the electrolyte membrane (this is hereafter called "electrolyte membrane non-constructing a bridge") of the mold non-constructing a bridge was obtained by changing into a proton mold.

[0087] (Example 2 of a comparison) The perfluoro system bridge formation film was produced using the approach similar to the bridge formation approach indicated by U.S. Pat. No. 57414087. That is, p-amino thinner MIKKU ester (20-mol% [as opposed to / Sulfonyl full ora

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id / a radical] was made to react to the PFSF film (however, a sulfonyl full ora id concentration: 9.07×10^{-4} mol/g of a radical, thickness : 50 micrometers).

[0088] Then, UV irradiation was carried out to the obtained film, and p-amino thinner MIKKU ester was made to construct a bridge, and it considered as the bridge formation film. subsequently, the obtained bridge formation film -- 25% sodium-hydroxide water solution -- 90 degrees C -- heat-treating -- hydrolyzing -- a sulfonyl full ora -- the id -- the radical was changed into the sulfonic-acid sodium group. Furthermore, reflux processing of 1 hour was repeated twice in 1-N sulfuric-acid water solution, and the polyelectrolyte film (this is hereafter called "non-strong acid nature bridge formation electrolyte membrane") over which the bridge was constructed by the non-strong acid nature bridge formation radical was obtained by changing into a proton mold.

[0089] (Example 3 of a comparison) a sulfonyl full ora -- the id -- according to the same procedure as the example 2 of a comparison, the non-strong acid nature bridge formation electrolyte membrane was produced to the radical except having used two-mol% p-amino thinner MIKKU ester.

[0090] (Example 4 of a comparison) a sulfonyl full ora -- the id -- according to the same procedure as the example 2 of a comparison, the non-strong acid nature bridge formation electrolyte membrane was produced to the radical except having used 40-mol% p-amino thinner MIKKU ester.

[0091] (Example 5 of a comparison) a sulfonyl full ora -- the id -- according to the same procedure as the example 1 of a comparison, the electrolyte membrane non-constructing a bridge was produced except having used the PFSF film whose concentration of a radical is 1.25×10^{-3} mol/g.

[0092] (Example 6 of a comparison) According to the example 1 of JP,9-263637,A, the polymer which has a unit ($-\text{SO}_2\text{CF}_2\text{CONLi}-$) was compounded, the ion exchange was carried out to the pan with 1M sulfuric acid, the polymer of a mold ($-\text{SO}_2\text{CF}_2\text{CONH}-$) was obtained, and the solubility over water was investigated.

[0093] The conductivity of the equivalent weight and the film showing the weight of the polymer per 1Eq of acids and the creep resistance in 200 degrees C were evaluated about the strong acid nature bridge formation electrolyte membrane obtained in the examples 1-5, the electrolyte membrane obtained in the examples 1 and 5 of a comparison non-constructing a bridge, and the non-strong acid nature bridge formation electrolyte membrane obtained by the list in the examples 2-4 of a comparison. Moreover, the solubility over the water was investigated about the example 6 of a comparison. In addition, the creep test approach is as follows at the measuring method of equivalent weight and conductivity, and a list.

[0094] Measurement of equivalent weight: 1 evening vacuum drying of the obtained film was first carried out at 100 degrees C, and membranous dry weight (Wdry) was measured. Subsequently, after it was immersed for about 10 minutes at 50 degrees C into 1N HCl water solution and ion exchange water washed the dried film, it was immersed for about 10 minutes at 50 degrees C into 2N NaCl water solutions. Furthermore, the neutralization titration of the amount of hydrogen ions emitted into the NaCl water solution was carried out using 1N NaOH water solution, and membranous equivalent weight was found by the several 1 following formula. In addition, MCI automatic titrator GT-05 were used for the neutralization titration.

[0095]
[Equation 1] (Equivalent weight) = $W_{\text{dry}} / f \times N \times V$, however Wdry : Membranous dry weight (g)
f : NaOH Factor N of a water solution : Normality of a NaOH water solution (N)
V : volume of the NaOH water solution which neutralization took (l)

[0096] Measurement of conductivity: It was immersed into pure water as pretreatment, the obtained film was cut down in the state of swelling by width-of-face [of 1cm] x die length of 1.2cm, and the conductivity measurement cel of two terminals was equipped with it. In addition, the platinum foil which carried out platinum black plating for the improvement in contact with the film was used for the current and the electrical-potential-difference terminal of a cel.

[0097] Subsequently, this cel was sunk into 25-degree C pure water, and it asked for membrane resistance with the alternating current anodizing process (10kHz of test frequencies) using the LCR meter (4262made from YHP A LCR METER), and asked for

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conductivity (σ) by the several 2 following formula. In addition, the value measured by the micrometer was used for thickness after conductivity measurement.

[0098] [Equation 2] $\sigma = l/R - A = l/R - w - t$, however σ : Conductivity (S/cm)

R: Resistance (Ω)

l: Distance between electrical-potential-difference terminals (= 1)

A: The membranous cross section (cm²)

t: Thickness (cm)

w: Film width (cm)

[0099] The creep test-proof in 200 degrees C: The spindle was hung on the film, it exposed to the 200-degree C ambient atmosphere, and the time amount from which the film is extended and die length doubles was measured so that a load might become 100 ton/m².

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[Procedure revision]
[Filing Date] February 1, Heisei 13 (2001. 2.1)
[Procedure amendment 1]
[Document to be Amended] Specification
[Item(s) to be Amended] Claim
[Method of Amendment] Modification
[Proposed Amendment]
[Claim(s)]
[Claim 1] The high thermally stable polymer electrolyte characterized by constructing the bridge over a perfluoro system high molecular compound through a strong acid nature bridge formation radical.
[Claim 2] The high thermally stable polymer electrolyte according to claim 1 characterized by said strong acid nature bridge formation radical being at least one chosen from bis-sulfonylimide, sulfonyl carbonyl imide, bis-carbonyl imide, and bis-sulfonyl methylene.
[Claim 3] The electrochemistry device using a high thermally stable polymer electrolyte according to claim 1 or 2.
[Claim 4] The fuel cell using a high thermally stable polymer electrolyte according to claim 1 or 2.
[Claim 5] Water electrolysis equipment using a high thermally stable polymer electrolyte according to claim 1 or 2.

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[Claim 6] The halide acid electrolytic device using a high thermally stable polymer electrolyte according to claim 1 or 2.

[Claim 7] Brine electrolysis equipment using a high thermally stable polymer electrolyte according to claim 1 or 2.

[Claim 8] The hydrogen and/or the oxygen enricher using a high thermally stable polymer electrolyte according to claim 1 or 2.

[Claim 9] The humidity sensor using a high thermally stable polymer electrolyte according to claim 1 or 2.

[Claim 10] The gas sensor using a high thermally stable polymer electrolyte according to claim 1 or 2.

[Procedure amendment 3]

[Document to be Amended] Specification

[Item(s) to be Amended] The name of invention

[Method of Amendment] Modification

[Proposed Amendment]

[Title of the Invention] A high thermally stable polymer electrolyte and the electrochemistry device using this

[Procedure amendment 4]

[Document to be Amended] Specification

[Item(s) to be Amended] 0001

[Method of Amendment] Modification

[Proposed Amendment]

[0001]

[Field of the Invention] This invention relates to the electrochemistry device using a high thermally stable polymer electrolyte and this suitable as an electrolyte membrane used for a fuel cell, water electrolysis equipment, a halide acid electrolytic device, brine electrolysis equipment, hydrogen and/or an oxygen enricher, a humidity sensor, a gas sensor, etc. in more detail about the electrochemistry device which used a high thermally stable polymer electrolyte and this.

[Procedure amendment 5]

[Document to be Amended] Specification

[Item(s) to be Amended] 0115

[Method of Amendment] Modification

[Proposed Amendment]

[0115] The application of the high thermally stable polymer electrolyte concerning this invention is not limited to a fuel cell or an SPE electrolytic device, can be used also as an electrolyte used for various kinds of electrochemistry devices, such as a halide acid electrolytic device, brine electrolysis equipment, hydrogen and/or an oxygen enricher, a humidity sensor, and a gas sensor, and, thereby, can acquire the same effectiveness as the gestalt of the above-mentioned implementation from the above thing.

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(54) 【発明の名称】 高耐熱性高分子電解質

(57) 【要約】

【課題】 耐熱性、耐酸化性、及び導電性に優れた高耐熱性高分子電解質を提供すること。

【解決手段】 スルホニルハライド基等、強酸性架橋基となりうる官能基を備えたパーフルオロ系高分子化合物同士、あるいは、このようなパーフルオロ系高分子化合物に、分子の末端にスルホンアミド等の強酸性架橋基となりうる官能基を備えた架橋剤を加え、これらを架橋反応させることにより、パーフルオロ系高分子化合物をビススルホニルイミド等からなる強酸性架橋基で架橋する。

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【特許請求の範囲】

【請求項1】 強酸性架橋基を介して、パーフルオロ系高分子化合物が架橋されていることを特徴とする高耐熱性高分子電解質。

【請求項2】 前記強酸性架橋基が、ビススルホニルイミド、スルホニルカルボニルイミド、ビスカルボニルイミド、ビススルホニルメチレンから選ばれた少なくとも1つであることを特徴とする高耐熱性高分子電解質。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、高耐熱性高分子電解質に関し、さらに詳しくは、燃料電池、水電解、ハロゲン化水素酸電解、食塩電解、酸素濃縮器、湿度センサ、ガスセンサ等に用いられる電解質膜等として好適な高耐熱性高分子電解質に関するものである。

【0002】

【従来の技術】固体高分子電解質は、高分子鎖中にスルホン酸基等の電解質基を有する固体高分子材料であり、特定のイオンと強固に結合したり、陽イオン又は陰イオンを選択的に透過する性質を有していることから、粒子、繊維、あるいは膜状に成形し、各種の用途に利用されている。

【0003】例えば、固体高分子型燃料電池は、電解質膜の両面に一對の電極を設け、改質ガス等の水素を含む燃料ガスを一方の電極（燃料極）へ供給し、空気等の酸素を含む酸化剤ガスを他方の電極（空気極）へ供給し、燃料が酸化する際に発生する化学エネルギーを、直接電気エネルギーとして取り出す電池である。固体高分子型燃料電池には、電解質膜として、プロトン伝導性を有する固体高分子電解質膜が用いられている。

【0004】また、SPE電解法は、水を電気分解することにより水素と酸素を製造する方法であり、電解質として、従来のアルカリ水溶液に代えて、プロトン伝導性を有する固体高分子電解質膜が用いられている。

【0005】このような用途に用いられる固体高分子電解質としては、例えば、ナフィオン（登録商標、デュボン社製）に代表される非架橋のパーフルオロ系電解質が知られている。パーフルオロ系電解質は、化学的安定性が非常に高いことから、燃料電池、SPE電解等、過酷な条件下で使用される電解質膜として賞用されているものである。

【0006】また、米国特許第5741408号には、芳香族ポリエーテルケトンにスルホニルハライド基を導入し、導入されたスルホニルハライド基とUV効果型のアミン系架橋剤とを反応させ、次いでアミン系架橋剤を架橋反応させることにより得られる架橋型炭化水素系電解質膜が開示されている。

【0007】さらに、ジャーナル・オブ・フルオリン・ケミストリ（Journal of Fluorine Chemistry）第72巻（1995年）203～208頁、及びジャーナル・オ

ブ・エレクトロケミカル・ソサイアティ（Journal of Electrochemical Society）第145巻、No. 1（1998年）107～109頁には、新規な酸基として、ビス（パーフルオロアルキルスルホニル）イミド基が提案されており、強酸性を呈する種々のビス（パーフルオロアルキルスルホニル）イミドポリマ、ビス（パーフルオロアルキルスルホニル）イミド化合物が報告されている。また、特開平9-263637号公報には、スルホニルカルボニルイミドアニオンが高濃度で含有された重合体が開示されている。

【0008】

【発明が解決しようとする課題】ところで、固体高分子型燃料電池は、電池の作動温度が高くなるほど、発電効率が高くなることが知られている。また、固体高分子電解質の両面に接合される電極には、白金系の電極触媒が含まれているが、白金は、微量の一酸化炭素であっても被毒され、燃料電池の出力を低下させる原因となる。しかも、電極触媒の一酸化炭素による被毒は、低温ほど著しくなることが知られている。

【0009】そのため、メタノール改質ガス等、微量の一酸化炭素を含むガスを燃料ガスとして用いる固体高分子型燃料電池においては、高効率化と電極触媒の一酸化炭素被毒の低減のために、作動温度を高くすることが望まれている。

【0010】また、水電解において、水の電気分解に必要な全エネルギーは温度によってさほど変化しないが、水の電気分解に必要な最低の電圧、すなわち理論分解電圧は、高温になるほど小さくなることが知られている。そのため、外部から熱エネルギーを系に供給し、高温において電気分解反応を行わせることができれば、高価な電気エネルギーの消費を減らすことができ、効率の点で有利である。

【0011】しかしながら、ナフィオンに代表されるパーフルオロ系電解質は、非架橋であるために耐熱性が低く、ガラス転移温度近傍である130℃以上でクリープするという性質がある。そのため、パーフルオロ系電解質を燃料電池やSPE電解装置に用いた場合には、作動温度を100℃以下とする必要があり、一酸化炭素による電極触媒の被毒の防止や効率の点で有利な高温で使用するできないという問題があった。また、パーフルオロ系電解質は、非架橋であるため、導電性を向上させるために電解質基の導入量を増しすぎると、水に著しく膨潤、もしくは可溶化してしまい、膜の設計自由度も大幅に限定されていた。

【0012】一方、パーフルオロ系電解質を架橋することができれば、高温における高分子鎖の流動が抑制されるので、パーフルオロ系電解質の耐高温クリープ化に対して有効と考えられる。さらには、架橋により膜の電解質基の導入量を増しても可溶化することなく、導電性の向上など、その設計自由度が向上する。しかしながら、

パーフルオロ系電解質は、構造の化学的安定性ゆえに、主鎖での架橋は難しい。

【0013】これに対し、米国特許第5741408号に開示されている方法を転用し、パーフルオロ系電解質に備えられており、かつ反応性の高い電解質基もしくは電解質基前駆体とアミン系架橋剤とを反応させれば、パーフルオロ系電解質を架橋させることも可能である。しかしながら、この方法では、パーフルオロ系電解質に含まれる電解質基の量が少なくなり、導電性が低下するという問題がある。

【0014】また、米国特許第5741408号に開示されている架橋型炭化水素系電解質自体は、架橋剤を含めて主要部分が炭化水素構造で構成されているために、高温での耐酸化性がなく、そのままでは高温で使用することはできない。

【0015】さらに、ジャーナル・オブ・エレクトロケミカル・ソサイエティ第145巻、No. 1 (1998年) 107~109頁には、ビス(パーフルオロアルキルスルホニル)イミド基とナフィオン様のパーフルオロ骨格を組み合わせることににより、ナフィオンとほぼ同様のプロトン伝導性を有するビス(パーフルオロアルキルスルホニル)イミドポリマが得られることが報告されている。しかしながら、これらの化合物は、いずれも非架橋型の化合物であるので、ナフィオンと同様に、耐熱性に問題がある。また、こうした官能基をパーフルオロ系電解質の架橋に応用した例はない。

【0016】また、特開平9-263637号公報に示された重合体(H⁺タイプ)は、高濃度で強酸基を含有するため、基本的には水に可溶であり、燃料電池用の電解質としては、耐熱性以前に、そのままで使用できるものではない。

【0017】本発明が解決しようとする課題は、耐熱性、及び耐酸化性に優れ、しかも高い導電性を有する高耐熱性高分子電解質を提供することにある。

【0018】

【課題を解決するための手段】上記課題を解決するために本発明に係る高耐熱性高分子電解質は、強酸性架橋基を介して、パーフルオロ系高分子化合物が架橋されていることを要旨とするものである。

【0019】ここで、強酸性架橋基とは、架橋後の架橋点の構造が、水を含んだ状態で強酸性を呈するものをいう。このような性質を有する架橋基としては、種々の構造を有するものが挙げられるが、強酸性架橋基としては、ビススルホニルイミド、スルホニルカルボニルイミド、ビスカルボニルイミド、ビススルホニルメチレンなどが好適である。なお、架橋点は、パーフルオロ系高分子化合物の分子鎖中のいずれかにあれば良く、特に限定されるものではない。

【0020】本発明に係る高耐熱性高分子電解質は、強酸性架橋基を介してパーフルオロ系高分子化合物が架橋

されているので、高温における分子の流動が抑制され、耐高温クリープ性を大幅に向上させることができる。

【0021】また、架橋点そのものが強酸性であるため、架橋密度を増加させても、電解質の導電性を大きく低下させることがない。さらに、高分子鎖がパーフルオロ系で構成されているため、高温における耐酸化性も問題とならない。

【0022】そのため、これを例えば燃料電池やSPE電解装置に用いた場合には、130℃以上の高温条件下であっても安定に作動でき、効率を飛躍的に向上させることができる。しかも、メタノール改質型燃料電池において問題となっている、電極触媒の一酸化炭素による被毒に起因する電圧低下は、こうした高温運転により大幅に軽減することができる。

【0023】

【発明の実施の形態】以下、本発明の実施の形態を詳細に説明する。本発明に係る高耐熱性高分子電解質は、強酸性架橋基と、強酸性架橋基を介して架橋されたパーフルオロ系高分子化合物とを備えている。

【0024】ここで、強酸性架橋基とは、上述したように、架橋後の架橋点の構造が強酸性を呈するものをいい、架橋前の官能基が、必ずしも強酸性である必要はない。パーフルオロ系高分子化合物を架橋させるための強酸性架橋基としては、具体的には、ビススルホニルイミド(-SO₂-NH-SO₂-)が好適である。

【0025】ビススルホニルイミドは、パーフルオロ骨格と組み合わせることにより、ナフィオンと同等の高いプロトン伝導性を発現する。これは、ビススルホニルイミドを介してパーフルオロ系高分子化合物を架橋させることにより、N-H結合に寄与する電子が、電気陰性度の大きなFに引っ張られてパーフルオロ骨格側に移動し、架橋点に結合しているHがプロトンとして放出されやすくなるためである。

【0026】従って、パーフルオロ系高分子を架橋させるための強酸性架橋基は、ビススルホニルイミドに限られるのではなく、架橋点から電子を移動させやすい構造を備えた架橋基であれば、いずれも本発明で言う「強酸性架橋基」となり得る。

【0027】強酸性架橋基の他の好適な一例としては、例えば、ビススルホニルメチレン(-SO₂-CH₂-SO₂-)、ビスカルボニルイミド(-CO-NH-CO-)、スルホニルカルボニルイミド(-CO-NH-SO₂-)等が挙げられる。

【0028】本発明に係る高耐熱性高分子電解質の主要部分を構成するパーフルオロ系高分子化合物の構造は、特に限定されるものではないが、スルホン酸基、カルボン酸基、ビススルホニルイミド基、ホスホン酸基などの強酸性官能基を側鎖に有するパーフルオロ系電解質ポリマ、あるいはその前駆体や誘導体などが特に好適である。また、その高分子鎖は、直鎖状、あるいは分岐状の

いずれの構造を有するものであっても良い。また、架橋点は、パーフルオロ系高分子化合物の分子鎖中のいずれかにあれば良い。すなわち、主鎖で架橋されていても良く、側鎖で架橋されていても良い。

【0029】なお、本発明の場合、架橋密度が大きくなるほど、耐熱性に優れた高分子電解質が得られるが、架橋密度が過大になると、含水及び水分子の移動を妨げ、かえってプロトン導電性を低下させる傾向がある。従って、架橋密度は、高耐熱性高分子電解質に要求される耐熱性、導電性等に応じて、最適な値を選択すればよい。

【0030】また、本発明に係る高耐熱性高分子電解質は、1種類の強酸性架橋基を介して、パーフルオロ系高分子化合物が架橋されていても良く、あるいは、2種以上の強酸性架橋基を介して、パーフルオロ系高分子化合物が架橋されていても良い。

【0031】次に、本発明に係る高耐熱性高分子電解質の製造方法について説明する。本発明に係る高耐熱性高分子電解質は、パーフルオロ系高分子鎖同士を、直接、あるいは、架橋剤を介して架橋反応させることにより得ることができる。

【0032】従って、高耐熱性高分子電解質の主要部分を構成するパーフルオロ系高分子化合物には、パーフルオロ系高分子化合物を構成する分子鎖中のいずれかに、架橋剤と反応して強酸性架橋基となり得る官能基（以下、これを「官能基A」という）を備えている必要がある。

【0033】パーフルオロ系高分子化合物に備えられる官能基Aとしては、具体的には、スルホニルハライド基、カルボニルハライド基、カルボン酸エステル基等、及びこれらの誘導体が好適な一例として挙げられる。特に、スルホニルハライド基は、架橋に消費されなかった場合であっても、これを加水分解すれば容易に強酸基となり、電解質に高い導電率を付与することができるので、官能基Aとして好適である。

【0034】また、このような官能基Aを有するパーフルオロ系高分子化合物としては、具体的には、テトラフルオロエチレンとパーフルオロ（4-メチル-3, 6-ジオキサオクト-7-エン）スルホニルフルオリドの共重合体、テトラフルオロエチレンとパーフルオロ（3-オキサベンター-4-エン）スルホニルフルオリドとの共重合体、テトラフルオロエチレンとパーフルオロ（4-オキサヘキサ-5-エン）スルホニルフルオリドとの共重合体、テトラフルオロエチレンとパーフルオロ（4-オキサ-5-ヘキセノイルクロライド）との共重合体等、及びこれらの誘導体が好適な一例として挙げられる。

【0035】なお、パーフルオロ系高分子化合物に備えられる官能基Aの濃度は、特に限定されるものではなく、高耐熱性高分子電解質に要求される耐熱性、導電性等に応じて、最適な濃度を有する化合物を用いればよ

い。一般的には、官能基Aの濃度が高くなるほど、架橋密度の制御範囲が広がるので、耐熱性及び／又は導電性の異なる種々の高分子電解質が得られるという利点がある。一方、官能基Aの濃度が少なくなりすぎると、架橋密度が低下して、耐熱性が不十分となる。具体的には、官能基Aの濃度としては、 $4 \times 10^{-3} \text{ mol/g}$ $\sim 1 \times 10^{-6} \text{ mol/g}$ 、好ましくは $2 \times 10^{-3} \text{ mol/g} \sim 1 \times 10^{-6} \text{ mol/g}$ である。

【0036】また、架橋前のパーフルオロ系高分子化合物には、1種類の官能基Aが含まれていても良く、あるいは、2種以上の官能基Aが含まれていても良い。さらに、1種又は2種以上の官能基Aを有する単一のパーフルオロ系高分子化合物を架橋させてもよく、あるいは、同一又は異なる官能基Aを備えた2種以上のパーフルオロ系高分子化合物を任意の比率で混合し、これを架橋させても良い。

【0037】次に、架橋剤について説明する。架橋剤としては、1分子中に、パーフルオロ系高分子化合物が有する官能基Aと反応して架橋することが可能な2以上の官能基を備え、しかも、その内の少なくとも1つが、強酸性架橋基となり得る官能基（以下、これを「官能基B」という）からなるものを用いる必要がある。特に、1つの分子中に、上述のような官能基Bを2個以上備えているものが、架橋剤として好適である。

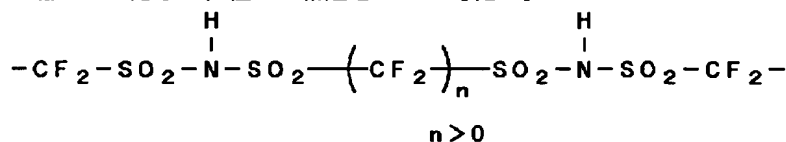
【0038】架橋剤に備えられる官能基Bとしては、具体的には、スルホンアミド基（ $\text{NH}_2 - \text{SO}_2 -$ ）、スルホニル（N-トリメチルシリル）イミドナトリウム塩（ $(\text{CH}_3)_3\text{Si} - \text{N}(\text{Na}) - \text{SO}_2 -$ ）、アミド基（ $\text{NH}_2 - \text{CO} -$ ）等、及びこれらの誘導体が好適な一例として挙げられる。但し、スルホニル（N-トリメチルシリル）イミドナトリウム塩については、ナトリウムでなくとも、アルカリ金属やアルカリ土類金属、水素でも良い。

【0039】また、このような官能基Bを備えた架橋剤としては、具体的には、パーフルオロ-1, 4-ジスルホンアミドブタン、また、そのN-トリメチルシリル化したナトリウム塩、パーフルオロ-1, 4-ジアミドブタン、アンモニア、ビス（トリメチルシリル）アミドリチウム等、及びこれらの誘導体が好適な一例として挙げられる。もちろん、架橋剤中にパーフルオロアルキレン基がある場合、その炭素数nは、 $n \geq 1$ であればいくつでも良く、途中で分岐等があってもかまわない。さらに、架橋剤は、官能基Bを側鎖に有した高分子化合物であってもよい。なお、パーフルオロ系高分子化合物が上記に挙げた官能基Bを有し、架橋剤が官能基Aを有しても、実質的に同じ効果を得ることができる。

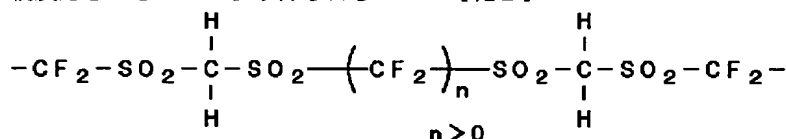
【0040】なお、架橋剤には、上述のような1種類の官能基Bが含まれていても良く、あるいは、2種以上の官能基Bが含まれていても良い。また、1種又は2種以上の官能基Bを備えた単一の化合物を架橋剤として用い

でも良く、あるいは、同一又は異なる官能基Bを備えた2種以上の化合物を任意の比率で混合し、これを架橋剤として用いても良い。

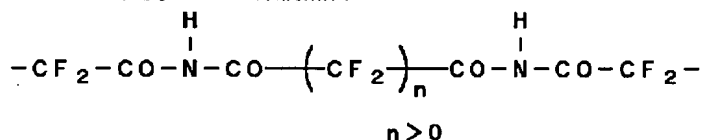
【0041】上述のような官能基Aを備えたパーフルオロ系高分子化合物を用い、これに官能基Bを備えた適当な架橋剤を加え、常法を用いて架橋反応させると、官能基A及び官能基Bの組み合わせに応じて、種々の構造を*



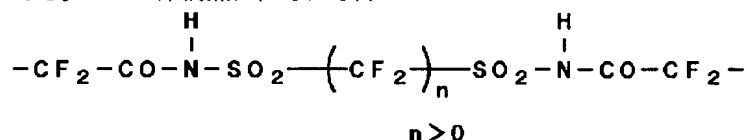
【0043】化1の式に示す架橋構造は、分子の両端にスルホンアミド基もしくはそのトリメチルシリル化ナトリウム塩を有するパーフルオロ系架橋剤と、分子鎖中のいずれかにスルホニルハライド基を有するパーフルオロ系高分子化合物とを架橋反応させることにより得られる※



【0045】また、化2の式に示す架橋構造は、分子の両端にスルホニルメチレンリチウム基を有するパーフルオロ系架橋剤と、分子鎖中のいずれかにスルホニルハライド基を有するパーフルオロ系高分子化合物とを架橋反応させることにより得られるものである。2つの架橋点★



【0047】また、化3の式に示す架橋構造は、分子の両端にカルボニルアミド基を有するパーフルオロ系架橋剤と、分子鎖中のいずれかにカルボニルハライド基を有するパーフルオロ系高分子化合物とを架橋反応させることにより得られるものである。2つの架橋点は、それぞれ☆



【0049】さらに、化4の式に示す架橋構造は、分子の両端にスルホンアミド基もしくはそのトリメチルシリル化ナトリウム塩を有するパーフルオロ系架橋剤と、分子鎖中のいずれかにカルボニルハライド基を有するパーフルオロ系高分子化合物とを架橋反応させることにより得られるものである。2つの架橋点は、それぞれ、強酸性架橋基であるスルホニルカルボニルイミド(−CO−NH−SO₂−)になっている。

※有する強酸性架橋基で架橋された高耐熱性高分子電解質が得られる。官能基Aを備えたパーフルオロ系高分子化合物と、官能基Bを備えた架橋剤を架橋反応させることにより得られる強酸性架橋基の構造の一例を、次の化1〜化4の式に示す。

【0042】

【化1】

※ものである。2つの架橋点は、それぞれ、強酸性架橋基であるビススルホニルイミド(−SO₂−NH−SO₂−)になっている。

【0044】

【化2】

★は、それぞれ、強酸性架橋基であるビススルホニルメチレン(−SO₂−CH₂−SO₂−)になっている。

【0046】

【化3】

☆は、それぞれ、強酸性架橋基であるビスカルボニルイミド(−CO−NH−CO−)になっている。

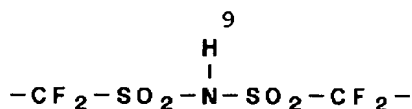
【0048】

【化4】

【0050】また、官能基Aを備えたパーフルオロ系高分子化合物と、官能基Bを備えたパーフルオロ系高分子化合物を架橋反応させることにより得られる強酸性架橋基の構造の一例を、次の化5〜化8の式に示す。

【0051】

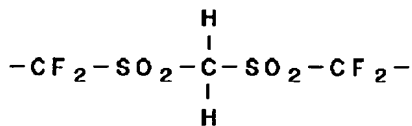
【化5】



【0052】化5の式に示す架橋構造は、分子鎖中のいずれかにスルホニルハライド基を有するパーフルオロ系高分子化合物と、分子鎖中のいずれかにスルホンアミド基もしくはそのトリメチルシリル化ナトリウム塩を有するパーフルオロ系高分子化合物とを架橋反応させることにより得られるものである。2つの高分子化合物は、1つの架橋点で架橋されており、架橋点は、強酸性架橋基であるビススルホニルイミド（ $-\text{SO}_2-\text{NH}-\text{SO}_2-$ ）になっている。

【0053】

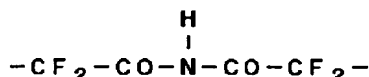
【化6】



【0054】また、化6の式に示す架橋構造は、分子鎖中のいずれかにスルホニルハライド基を有するパーフルオロ系高分子化合物と、分子鎖中のいずれかにスルホニルメチレンリチウム基を有するパーフルオロ系高分子化合物とを架橋反応させることにより得られるものである。2つの高分子化合物は、1つの架橋点で架橋されており、架橋点は、強酸性架橋基であるビススルホニルメチレン（ $-\text{SO}_2-\text{CH}_2-\text{SO}_2-$ ）になっている。

【0055】

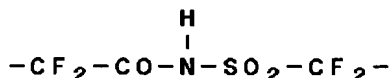
【化7】



【0056】また、化7の式に示す架橋構造は、分子鎖中のいずれかにアミド基を有するパーフルオロ系高分子化合物と、分子鎖中のいずれかにカルボニルハライド基を有するパーフルオロ系高分子化合物とを架橋反応させることにより得られるものである。2つの高分子化合物は、1つの架橋点で架橋されており、架橋点は、強酸性架橋基であるビスカルボニルイミド（ $-\text{CO}-\text{NH}-\text{CO}-$ ）になっている。

【0057】

【化8】



【0058】さらに、化8の式に示す架橋構造は、分子鎖中のいずれかにカルボニルハライド基を有するパーフルオロ系高分子化合物と、分子鎖中のいずれかにスルホンアミド基もしくはそのトリメチルシリル化ナトリウム塩を有するパーフルオロ系高分子化合物とを架橋反応さ

10

せることにより得られるものである。2つの高分子化合物は、1つの架橋点で架橋されており、架橋点は、強酸性架橋基であるスルホニルカルボニルイミド（ $-\text{CO}-\text{NH}-\text{SO}_2-$ ）になっている。この場合、反応の組み合わせにより、化7の式や化5の式に示した架橋基が生じる場合もある。

【0059】なお、化5の式、化7の式、及び化8の式の架橋構造は、カルボニルハライドやスルホニルハライドを有するパーフルオロ系高分子化合物と、アンモニアやビス（トリメチルシリル）アミドリチウムなどの金属塩と反応させることによって形成させてもよい。

【0060】これらの強酸性架橋基は、いずれも、本発明の目的である耐熱性の高い電解質を供することができるが、この中でも、ビススルホニルイミド基が熱安定性の点で特に優れている。

【0061】パーフルオロ系高分子化合物の官能基Aに対する架橋剤中の官能基Bのモル数比は、電解質に要求される耐熱性や導電性によって選べばよい。一般的には、（官能基Bのモル数）／（官能基Aのモル数）は、0.00001から1.0であり、さらに好ましくは、0.00005から0.8、より好ましくは0.0001から0.5である。ここで、このモル比が小さすぎると、架橋が不十分で耐熱性を付与できない。また、モル比が大きすぎると、架橋が進みすぎ、含水量が低下したり、水の移動が妨げられたりして、導電性が低下してしまう場合がある。

【0062】次に、本発明に係る高耐熱性高分子電解質の作用について説明する。本発明に係る高耐熱性高分子電解質は、強酸性架橋基を介してパーフルオロ系高分子化合物が架橋されているので、これをガラス転移温度以上の高温で使用した場合であっても、高分子鎖の流動が抑制される。そのため、非架橋型のパーフルオロ系高分子電解質と比較して、耐高温クリープ性が向上する。

【0063】また、非架橋型のパーフルオロ系電解質の場合、電解質基の濃度が過大になると、水に著しく膨潤し、電解質がゲル化、さらには水に可溶化する場合があるが、本発明に係る高耐熱性高分子電解質は、架橋構造を有しているので、電解質基の濃度が増大しても電解質がゲル化、もしくは可溶化しにくくなっている。そのため、非架橋型のパーフルオロ系電解質と比較して、電解質基の濃度を高くすることができ、高い導電性を有する電解質が得られるという利点がある。

【0064】さらに、架橋反応に供されるパーフルオロ系高分子化合物中の官能基Aが、同時にパーフルオロ系高分子化合物の電解質基、もしくはその前駆体、誘導体でもある場合には、パーフルオロ系高分子化合物中に1個の架橋構造を形成する毎に、高分子鎖に備えられる2個の官能基Aが消費される。そのため、米国特許第5741408号に示されたような従来の架橋方法では、架橋密度が増加するに伴い高分子中の電解質基の量が減少

11

し、得られる高分子化合物の導電性を低下させる原因となる。

【0065】しかしながら、本発明に係る高耐熱性高分子電解質は、架橋点が強酸性を呈する強酸性架橋基となるので、架橋密度を増加させても、従来の架橋方法に比較して、導電率の低下が少ない。

【0068】特に、分子内に2以上の官能基Bを備えた架橋剤を用いて架橋させた場合には、架橋により2個の強酸性架橋基を高分子化合物内に導入することができ、架橋反応に消費された官能基Aを強酸性架橋基で補うことができる。そのため、架橋密度を増加させても、導電率を非架橋型のパーフルオロ系高分子電解質と同等もしくは近い値に維持することも可能となる。

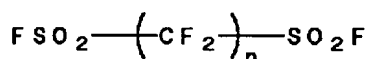
【００６７】しかも、本発明に係る高耐熱性高分子電解質の主要部分は、パーフルオロ系高分子化合物で構成されるので、高温における耐酸化性が問題となることもない。

【 0 0 6 8 】

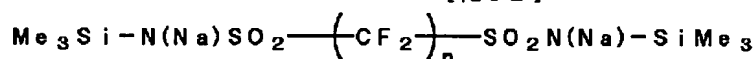
【実施例】（実施例１）初めに、以下の手順に従い、架橋剤を合成した。まず、架橋剤の原料として、両端末にスルホニルフルオリド基を有するパーフルオロ-１，４-ジスルホニルフルオリドブタンを用いた。パーフルオロ-１，４-ジスルホニルフルオリドブタンの化学式を、次の化９の式（ n は４）に示す。

【 0 0 6 9 】

【化9】



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【0076】次に、以下の手順に従い、架橋反応を行った。高耐熱性高分子電解質の原料となるパーフルオロ系高分子化合物には、加水分解前の電解質前駆体であるパーフルオロ系スルホンフルオライド膜（以下、これを「PF₆SF膜」という）を用いた。このPF₆SF膜のスルホンフルオライド基の濃度（ポリマ1g中のmol数）は 9.07×10^{-4} mol/g、膜厚は50 μ mである。架橋反応に用いたPF₆SF膜の化学式を、次の化13の式に示す。

【0077】

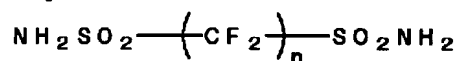
【化 1 3】

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*【0070】次に、化9の式に示すパーフルオロ-1，4-ジスルホンフルオリドブタンを、-78度にて過剰量の液体アンモニア中に加えてスルホンアミド化した。次いで、室温に戻してアンモニアを除去した後、塩化水素ガスを作用させ、両端末にスルホンアミド基を有するパーフルオロ-1，4-ジスルホンアミドブタンを合成した。得られたパーフルオロ-1，4-ジスルホンアミドブタンの化学式を、次の化10の式に示す。

【0071】

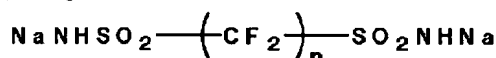
10 【化10】



【0072】次に、化10の式に示すスルホンアミド化合物をメタノールに溶解し、等量のナトリウムメトキシドを作用させ、スルホンアミドナトリウム塩を合成した。得られたスルホンアミドナトリウム塩の化学式を、次の化11の式に示す。

【0073】

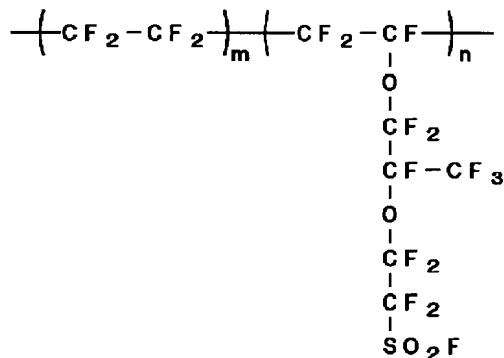
【化 1 1】



【0074】さらに、化11の式に示すスルホンアミドナトリウム塩に対し、アセトニトリル中で1.2倍量のヘキサメチルジシラザンを還流温度にて作用させ、目的の架橋剤を合成した。得られた架橋剤の化学式を、次の化12の式に示す。

【0075】

【化 1 2】



【0078】まず、化13の式に示すPFSF膜に含まれるスルホンフルオライド基に対して10mol%（架橋剤中の官能基ベースで20mol%）に相当する架橋剤をアセトニトリル中に溶解させた。次いで、架橋剤を溶解させたアセトニトリル中にPFSF膜を浸漬し、そのまま20時間加熱して、架橋膜とした。

【0079】次に、得られた架橋膜を25%水酸化ナトリウム水溶液で90℃に加熱処理して加水分解し、残留するスルホン基をスルホン酸ナトリウム

13

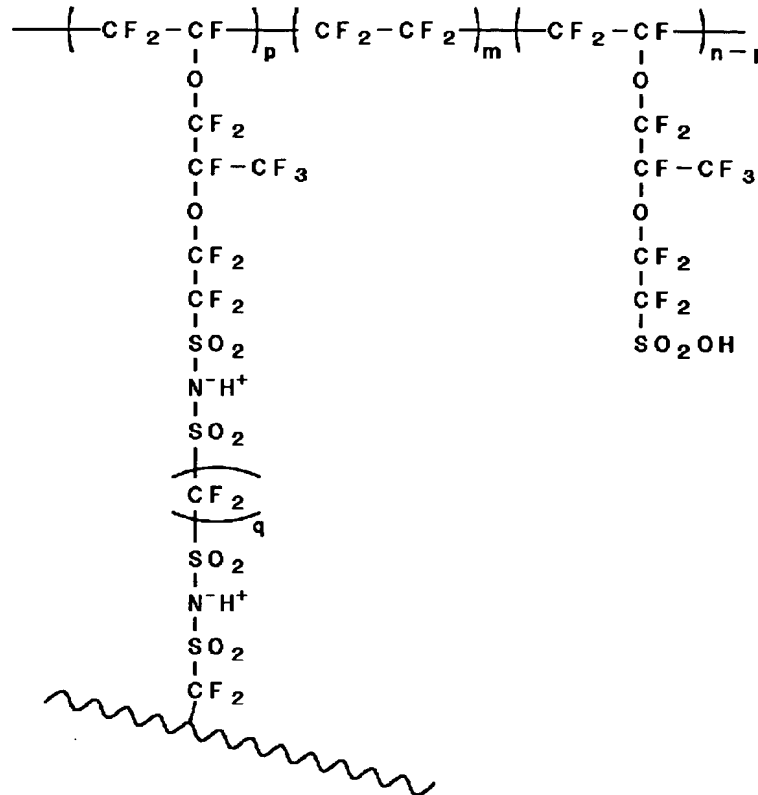
基に変換した。さらに、1 N硫酸水溶液で1時間の還流処理を2回繰り返し、プロトン型に変換することにより、強酸性架橋基で架橋された高分子電解質膜（以下、これを「強酸性架橋電解質膜」という）を得た。得られ*

14

*た強酸性架橋電解質膜の化学式を、次の化14の式に示す。

【0080】

【化14】



【0081】なお、化14式は、テトラフルオロエチレンからなる主鎖に重合しているn個の側鎖の内、p個が架橋に消費された状態を模式的に示したものである。また、化14式中、波線で示した部分は、化13の式と同様の構造を有するパーフルオロ系高分子鎖を略示したものである。

【0082】（実施例2）スルホンフルオライド基に対して、1 mol %の架橋剤（官能基ベースで2 mol %）を用いた以外は、実施例1と同様の手順に従い、強酸性架橋電解質膜を作製した。

【0083】（実施例3）スルホンフルオライド基に対して20 mol %の架橋剤（官能基ベースで40 mol %）を用いた以外は、実施例1と同様の手順に従い、強酸性架橋電解質膜を作製した。

【0084】（実施例4）スルホンフルオライド基の濃度が 1.25×10^{-3} mol / gであるPF SF膜を用いた以外は、実施例1と同様の手順に従い、強酸性架橋電解質膜を作製した。

【0085】（実施例5）架橋剤として、 $(\text{CH}_3)_3\text{Si}-\text{N}(\text{Na})-\text{Si}(\text{CH}_3)_3$ をスルホンフルオライド基に対して10 mol %用いた以外は、実施例3と同様の手順に従い、強酸性架橋電解質膜を作製し

た。

30 【0086】（比較例1）PF SF膜（但し、スルホンフルオライド基の濃度： 9.07×10^{-4} mol / g、膜厚：50 μm ）を、架橋させることなく、そのまま25%水酸化ナトリウム水溶液で90℃に加熱処理して加水分解し、スルホンフルオライド基をスルホン酸ナトリウム基に変換した。さらに、1 N硫酸水溶液で1時間の還流処理を2回繰り返し、プロトン型に変換することにより、非架橋型の電解質膜（以下、これを「非架橋電解質膜」という）を得た。

40 【0087】（比較例2）米国特許第57414087号で開示された架橋方法と類似の方法を用いて、パーフルオロ系架橋膜を作製した。すなわち、PF SF膜（但し、スルホンフルオライド基の濃度： 9.07×10^{-4} mol / g、膜厚：50 μm ）に対して、p-アミノシンナミックエステル（スルホンフルオライド基に対して20 mol %）を反応させた。

50 【0088】その後、得られた膜に対してUV照射し、p-アミノシンナミックエステルを架橋させ、架橋膜とした。次いで、得られた架橋膜を25%水酸化ナトリウム水溶液で90℃に加熱処理して加水分解し、スルホンフルオライド基をスルホン酸ナトリウム基に変換し